A STUDY OF CONTINUOUS POLYMERIZATION

BY

CHARLES JARCHOW DELBECQ

B. of Engr., University of Toledo, 1943

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY
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R. UNIV. BIBLIOTHEEK LEIDEN

A STUDY OF CONTINUOUS POLYMERIZATION

It is well known that the composition of copolymer is not in general identical with the compositon of the monomer mixture from which it is being formed. This fact and the short life of the growing polymer molecule give rise to the compositional heterogeneity which exists in a copolymer prepared in a batch process. It would be interesting to compare the properties of compositionally homogeneous and heterogeneous copolymers.

One method of obtaining a compositionally homogeneous copolymer is to carry out the polymerization in a continuous process (one in which the reactants are fed at a constant rate into a reactor, which is provided with efficient stirring, and the material in the reactor is removed at such a rate that the volume of material in the reactor remains constant), since such a system approaches a steady state in which the concentrations of reactants and products remain constant with time. Thus under steady state conditions the concentrations of the monomers remain constant and it is apparent that in principle a compositionally homogeneous copolymer would result from a bulk or solution polymerization carried out in a continuous process. However, because of the complexity of emulsion polymerization, it is not obvious that continuous copolymer obtained by using an emulsion system would display this same compositional homogeneity. Recent work by Wall and coworkers (1), cf. work and conclusions by Fordyce and coworkers (2), in which composition studies were made of copolymers obtained in a batch process using bulk, solution and emulsion systems, indicates the possibility that new monomers may be incorporated into an emulsion system in such a manner that they are uniformly distributed throughout the reaction locus. If this condition is realized then in the steady state the ratio of monomer concentrations will be constant throughout the reaction locus and the copolymer produced should be compositionally homogeneous.

In order to compare batch and continuous copolymer with respect to compositional heterogeneity the method of fractional precipitation was used to separate styrene-methyl methacrylate copolymer into composition fractions. The copolymer to be fractionated was dissolved in toluene and low boiling petroleum ether was added in increments to separate the copolymer into fractions. During the addition of each increment of precipitant the polymer solution was warmed to prevent precipitation and then the precipitation was effected by gradual cooling to a fixed temperature. The fractions thus obtained were in turn fractionated, in a similar manner, by the increment addition of methanol to the chloroform solution of the polymer. Analysis of selected fractions indicates the range of composition and hence the heterogeneity of the copolymer.

Batch and continuous emulsion copolymers of styrene and methyl methacrylate were fractionated and analyzed. At 77 per cent conversion the batch copolymer was found to be much more heterogeneous than the continuous copolymer. However the compositional heterogeneity which was observed in this continuous copolymer seemed too great to be caused by a statistical variation in composition from molecule to molecule. Further experiments showed this heterogeneity to be a function of conversion; the compositional heterogeneity of continuous copolymer obtained at 62 per cent conversion was found to be significantly less than the heterogeneity of continuous copolymer obtained at 77 per cent conversion. This dependence of compositional heterogeneity on conversion may be accounted for by the increase of the polymer to monomer ratio at the locus of reaction with increasing conversion. An increase in the ratio of polymer to monomer causes an increase in viscosity at the locus of reaction. A sufficient increase in viscosity prevents the uniform distribution of monomers throughout the reaction locus; as a result the free monomer ratio, and consequently the composition of copolymer being formed, varies appreciably from point to point within the locus of reaction.

It was found, in the case of continuous emulsion polymeri-

zation, that the conversion passes through a maximum and then decreases somewhat to a steady state value (observed for steady state conversions in the range 35-90 per cent). This observation seems to fit in quite well with Harkins' (3) picture of emulsion polymerization in which

1. Monomer diffuses from the oil droplets into the soap micelles.
2. The principle locus of reaction, the monomer-polymer particle, is initiated in this monomer which is solublized by the soap micelle.
3. The soap concentration, and consequently the micelle concentration and the rate of formation of monomer-polymer particles, decreases markedly with increasing conversion.

The maximum in the conversion curve is associated with the decrease in the rate of formation of monomer-polymer particles.

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VITA

The author was born in Toledo, Ohio, on August 19, 1921, and received his elementary and secondary education in the public schools of that city. He attended the University of Toledo from 1939 to 1943 and was graduated summa cum laude and received the degree of Bachelor of Engineering. In 1943 he entered the armed services and served as a meteorologist until 1946. In September, 1946, he entered the Graduate College of the University of Illinois. He was employed as a special research assistant under contract with the Rubber Reserve Corporation from February, 1946, to September, 1947, and again from June, 1948, to September, 1948, and held a University fellowship from October, 1947, to June, 1948, and again from September, 1948, to June, 1949.

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